The isothermal-isobaric ensemble

- Which extensive thermodynamic variables are constrained to have a particular value in the isothermal-isobaric ensemble.

- Give an expression for the probability of being in a microstate in the isothermal-isobaric ensemble

- Give an expression for the isothermal-isobaric partition function

- Give an expression for $\frac{\mathrm{d}S}{k_B}$ for the isothermal-isobaric ensemble that can be obtained using arguments based on statistical mechanics.

The isothermal-isobaric ensemble

- Give an expression for the Lagrange multiplier λ and explain how this result is derived.

- What thermodynamic potential can be calculated from the isothermal-isobaric partition function? How is this done and how is this result derived?

- Explain why: $1 = \sum_j e^{-\beta H(\mathbf{x}_j,\mathbf{p}_j)-\beta PV(\mathbf{x}_i,\mathbf{p}_i)-\Psi}$

- Now calculate the first derivative of $1 = \sum_j e^{-\beta H(\mathbf{x}_j,\mathbf{p}_j)-\beta PV(\mathbf{x}_i,\mathbf{p}_i)-\Psi}$ with respect to βP and hence show that $\langle V\rangle = -\frac{\partial\Psi}{\partial(\beta V)}$

The isothermal-isobaric ensemble

- Calculate the second derivative of $1 = \sum_j e^{-\beta H(\mathbf{x}_j,\mathbf{p}_j)-\beta PV(\mathbf{x}_i,\mathbf{p}_i)-\Psi}$ with respect to βP and hence show that $\langle (V-\langle V\rangle)^2\rangle = \frac{\partial^2 \Psi}{\partial(\beta P)^2}$

- Explain (in your own words) why $\langle (V-\langle V\rangle)^2\rangle = -\frac{\partial \Psi}{\partial(\beta P)}$.

- Use the chain rule to show that: $\frac{\partial\langle V\rangle}{\partial(\beta P)} = k_B T \frac{\partial \langle V\rangle}{\partial P}$ if T is constant.

- Use the result you have just arrived at to write an expression that tells you how the isothermal compressibility, κ_T, can be calculated from the fluctuations in the total volume $\langle (V-\langle V\rangle)^2\rangle$